

PRODUCTION AND SCREENING OF CARBON PRODUCT PRECURSORS FROM COAL

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INTRODUCTION

Because of its chemical constitution, coal has the potential to meet the requirements for a wide variety of carbon materials which are based on complex, aromatic hydrocarbons. The manufacture of carbon anodes for aluminum production, graphite electrodes for steel and other metal refining, high-quality pitches for carbon fibers, as well as carbonaceous binder and impregnation fluids is possible from coal through selection of processing conditions and solids separation.

The use of coal as a source of carbon materials is of some practical concern to the United States primarily for two reasons. The first concern is that the quality of imported and domestic petroleum-based precursors is steadily declining with sulfur and metals content expecting to continue to increase. Sulfur leads to environmental pollution and metals contribute to the degradation of coke performance. The second concern involves the availability of traditional sources of pitches. Some of these materials are derived as byproducts of metallurgical coke making in the recovery-coke oven. Because of environmental pressures, it is expected that no new coke plants will be built nor will significant upgrading of existing facilities occur in the foreseeable future in the United States. Consequently, it is anticipated that domestic production of coal-tar pitch will decrease by three percent per year over the next decade.

Researchers in the Chemical Engineering Department at West Virginia University (WVU) are involved in the production of kilogram quantities of coal-derived pitches and cokes for examination and evaluation by industry. Unlike conventional approaches, the coal-based precursors were obtained by extraction using N-methyl pyrrolidone (NMP) as a solvent. NMP is highly effective in rejecting mineral matter and inorganic sulfur contaminants while at the same time solubilizing a majority of the organic carbon in coal. These low-solids-containing materials were developed successfully into impregnation and binder pitches, anode-grade coke, and highly anisotropic graphite.

Recently, several specimens of coal-derived materials obtained by larger, "pilot plant" production were evaluated by WVU. These samples were provided by Consol and HTI. Emphasis is directed toward determining the suitability of the pitches as precursors for either binder pitch or anode quality coke. The results of testing of the coal-based materials by WVU will form the basis for the following discussion.

RESULTS

The first sample examined is a product of the Kerr-McGee critical solvent deasher (CSD), also known as the ROSE process. Although the CSD unit is no longer functioning, in 1979 it produced three streams at the Wilsonville, AL coal liquefaction plant. One stream was an ash concentrate, another a heavy-solvent-refined coal (SRC), and the third a light-stream SRC. The particular sample examined by WVU is the light-stream SRC. A summary of the data is presented in Table 1 along with data for a commercially available coal-tar binder pitch (CTP). The light-stream SRC was converted into green coke by heating to 600 °C and a specimen prepared for observation by polarized-light microscopy.

Table 1. Property values for the CSD light-stream SRC and a CTP

Material	Light-Stream SRC, Illinois Basin Coal	Coal-Tar Pitch
<u>Elemental Composition, wt%</u>		
C	85.71	93.83
H	6.73	3.92
N	1.80	0.92
S	0.68	0.59
⁺ O	5.08	0.74
C/H Atomic Ratio	1.06	1.99
¹ H _{aromatic} NMR, %	38.5	86.0
Density, g/cm ³	1.197	1.340
Softening Point, °C	133.5	110.3
Coke Yield, wt%	41.1	58.0
Toluene Insoluble, wt%	23.5	28.3
Ash Content, wt%	0.17	0.21

⁺oxygen by difference

Compared to the CTP, the light-stream SRC has a rather low aromaticity, low-coke yield, high-softening-point temperature, and high-oxygen content. These attributes combined would preclude the use of the light-stream SRC as a binder pitch. Moreover, the anisotropy in the green coke as evident by optical microscopy was judged to be of an insufficient development for use as an anode coke.

The second sample examined is representative of a two-stage direct coal liquefaction process stream. This product is a composite of individual samples taken over an extended time period identified as Run 259 made in 1990 at the Wilsonville integrated two-stage coal liquefaction pilot plant. Run 259 employed the use of catalysts in both stages of the reactor. Coal products were removed regularly at a point called the “interstage” which was located between the first and second reactors of the two-stage liquefaction system. After each sampling, the coal liquid was distilled to an atmospheric equivalent boiling point of 850 °F. The 850 °F+ fractions were combined to make a composite designated as R1235 which was evaluated by WVU.

As shown in Table 2, the high-ash content of R1235 (about 9 wt%) is presumably that indigenous to the coal and the catalytic additives. To produce a clean, low-ash material, sample R1235 was deashed by dissolving the coal product in N-methyl pyrrolidone. Simple filtration using a Buchner funnel and 1 µm filter paper was used to remove ash-forming constituents. The NMP was removed by rotary evaporation and the coal material vacuum dried overnight. This procedure revealed that R1235 was nearly 100 wt% soluble in NMP, with only the insoluble inorganic solids remaining on the filter paper. A summary of the available analyses before and after extraction with NMP is presented in Table 2. Samples of R1235 before and after NMP extraction were also converted into green coke and specimens prepared for observation by optical microscopy.

A comparison of the data in Table 2 with those of the CTP in Table 1 suggests that R1235 is a more suitable material for binder pitch because its carbon content, aromaticity, and coke yield are higher than the values for the light-stream SRC. However, the ash content of R1235 is nearly 9 wt%. This quantity of inorganics would preclude the use of R1235 in most carbon product precursors. Indeed, the ash-forming materials are not only undesirable contaminants but also interfere with the development of anisotropy in the green coke. Optical microscopy showed that R1235 produced an optical texture similar to that found in metallurgical-grade coke and, therefore, not suitable in itself for anode coke making.

Table 2. Characteristics of coal liquid R1235 before and after extraction with NMP

Material	As Received R1235	R1235 After NMP Extraction
<u>Elemental Composition, wt%</u>	<u>MAF</u>	
C	90.12	--
H	6.19	--
N	1.15	--
S	1.50	--
⁺ O	1.04	--
C/H Atomic Ratio	1.21	--
¹ H _{aromatic} NMR, %	63.4	--
Density, g/cm ³	1.303	1.215
Softening Point, °C	152.6	151.8
Coke Yield, wt%	62.3	54.6
Toluene Insoluble, wt%	32.9	26.2
Ash Content, wt%	8.74	0.10

⁺oxygen by difference

On the other hand, removal of the inorganic material by NMP extraction produces a pitch-like substance more amenable to coke and binder pitch production than either the light-stream SRC or the as-received R1235. Optical microscopy indicates that the development of molecular alignment in the NMP-extracted coal liquid after carbonization to green coke is considerable, producing optical textures seen similarly in conventional anode cokes. Moreover, the ash content, coke yield, toluene insolubility, and anisotropic development of the NMP-extracted material are judged to be more in line with commercial pitch precursors.

The next sample examined by WVU was approximately 100 lbs of coal liquid bottoms sent by Hydrocarbon Technologies, Inc. (HTI). The as-received material is a thick, viscous liquid at room temperature. Some characterization data are provided in Table 3. The data indicate that the material is unsuitable for binder pitch or anode coke primarily because of the low-coke yield, low-softening point, and unacceptably high-ash content.

Table 3. Characteristics of as-received HTI coal liquid

Material	Run 227-102, Periods 17, 18, 19, and 20
Softening Point, °C	Room Temperature
Coke Yield, wt%	38.8
THF Insoluble, wt%	13.7
Toluene Insoluble, wt%	16.4
Ash Content, wt%	10.7

The low softening point temperature of the as-received material is most likely because of the presence of low molecular weight species present in significant quantity, probably from the liquefaction solvent. This solvent should be removed prior to further use. In order to increase the softening point temperature, the coal liquid was vacuum distilled. To accomplish this, a 1-L autoclave was modified to function as a distillation unit. Essentially, all service ports to the reactor were closed except for one, which was connected to a heated transfer line. The transfer line was attached to a

receiving vessel to collect distillate material. Finally, the receiving vessel was connected to a cold trap and vacuum pump.

About 600 mL of as-received coal liquid were sealed in the autoclave and a stirrer mechanism activated while the system was under vacuum. The reactor contents were brought to a temperature of 350 °C and distillation continued until about 250 mL of distillate were recovered. The reactor furnace was then removed and an external water quench initiated to bring the temperature of the system down rapidly to about 150 °C. The reactor was opened and the contents allowed to solidify before removal and weighing. The distilled product was characterized with the results presented in Table 4.

Table 4. Properties of distilled HTI coal liquid

Density, g/cm ³	1.374
Softening Point, °C	144.7
Coke Yield, wt%	67.0
THF Insoluble, wt%	23.3
Toluene Insoluble, wt%	31.1
Ash Content, wt%	18.7

Vacuum distillation in this instance produced an ash-laden coal liquid with a softening point temperature of about 145 °C and an ash content near 19 wt%. The high ash content also prevented the development of anisotropy in the green coke as is evident by optical microscopy.

A sample of the distilled coal liquid was mixed with boiling NMP in a 1:10 wt:vol ratio. The solution was filtered hot and the filtrate recovered by rotary evaporation. Both the insoluble residue and clean extract were vacuum dried overnight before weighing.

The properties of the distilled and NMP extracted HTI coal liquid are listed in Table 5. Mass balance consideration indicates that nearly 100 percent of the organic matter was brought into solution by NMP. Furthermore, the softening point temperature of 124.0 °C and density of 1.205 g/cm³, as well as solubility in tetrahydrofuran and toluene, are more in line with values for commercially available solids-free pitches. However the coke yield is somewhat low, perhaps because of residual liquefaction solvent. Perhaps more importantly, optical microscopy of the green coke from the extracted HTI coal liquid showed significantly enhanced growth of molecular alignment. The optical structures are not unlike those seen in commercially produced anode cokes.

Table 5. Characteristics of distilled and NMP-extracted HTI coal liquid

Yield of NMP Solubles, wt%	80.1
Density, g/cm ³	1.205
Softening Point, °C	124.0
Coke Yield, wt%	48.3
THF Insoluble, wt%	1.63
Toluene Insoluble, wt%	12.7
Ash Content, wt%	0.7

SUMMARY

The results obtained thus far seem to indicate that a coal-derived, pitch-like material can be developed for use as an anode coke precursor or binder pitch after removal of inorganic solids by NMP extraction. Properties of some of the coal materials are not unreasonable when compared to other types of available pitches. The molecular arrangement and the optical structures present in the green coke of the deashed coal liquid may be suitable for the production of carbon products, but more testing needs to be conducted to confirm this.

CURRENT WORK

WVU has now completed distillation of the large sample of HTI coal liquid with the assistance of an industrial partner. The distilled material is currently undergoing extraction and purification by NMP solvation to produce a sample of sufficient quantity for additional testing both at WVU and in commercial laboratories. We plan either to convert the deashed HTI material in our in-house coking reactor into green coke for anode production or to use the material directly as a binder pitch.

In addition, HTI has also sent other coal liquefaction products for evaluation by WVU. These materials include pressure filter liquids and pressure filter solids. The products will be examined as received and after NMP extraction to determine their suitability as precursors for carbon products.